

Appln No. 10/815,526
Amdt date September 28, 2007
Reply to Office action of August 2, 2007

REMARKS/ARGUMENTS

Claims 1-25 are now in the application. Claims 1, 9, 21, 22 and 23 have been amended. Claims 24 and 25 have been added. The Applicant respectfully requests reconsideration and allowance of the application in view of the amendments and the following remarks.

1. Claim Objections

The Examiner considers that claims 16 and 18 are improper as they do not further limit the subject-matter of a previous claim.

To overcome this objection, the Applicant has amended claim 1 by inserting two commas as follows :

"Process for forming a protective coating containing aluminum on the surface of a metal substrate in which the said substrate and a non-gaseous precursor containing aluminum are placed in contact, at a high temperature, with an atmosphere ... " (emphasis in bold and underline added.)

As amended, claim 1 thus clearly recites that the substrate and the precursor are placed in contact with an atmosphere and not that the substrate and the precursor are placed in contact (together). Thus, claims 16 and 18 are proper and not inconsistent with the base claim 1 as recited above.

2. Claim Rejections (35 USC §112)

The Examiner rejects claims 9, 16 and 17 under 35 USC § 112, second paragraph, as being indefinite.

The Examiner contends that claim 9 recites the limitations "the said element of the **metal** is nickel" and "the said intermetallic compound is β -NiAl". However, the Applicant respectfully notes that claim 9 actually recites that "the said element of the **substrate** is nickel".

In addition, the Applicant has amended claim 9 to depend from claim 8 instead of claim 7 to overcome the indefiniteness objection.

Concerning the indefiniteness rejections of claims 16 and 19, the Applicant respectfully notes that this rejection is now overcome with the amendment of claim 1 as discussed above.

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3. Claim Rejections (35 USC § 103)

The Examiner rejects claims 1-15 and 18-23 under 35 USC § 103 (a) as being unpatentable over Darolia (US Patent No. 6,273,678), and further in view of Wachtell et al. (US Patent No. 3,257,230).

Before addressing the merits of the rejection based on prior art, a brief description of the present application is provided. The present application is directed toward a process for forming a protective coating containing aluminum on the surface of a metal substrate in which the said substrate and a non-gaseous precursor containing aluminum are placed in contact, at a high temperature, with an atmosphere containing an active gas. The active gas reacts with the precursor to form a gaseous aluminum compound, which decomposes on contact with the metal substrate, thereby depositing aluminum metal on the metal substrate.

As mentioned on page 1 of the present application, such a process which is also known as "aluminization," or "activated cementation", can be used for diffusing alloy coatings of the Ni-Al type. The operating conditions of such a process are mentioned in the present application (see pages 1-4).

As also noted in the present application (see page 4, 2nd Paragraph), the favourable effect of zirconium on the bonding of a layer of oxide to a metal substrate was already known. However, no process which could be used industrially had been suggested for inserting this element (zirconium) into a protective coating containing aluminum.

As such, embodiments of the present invention are directed toward an improvement to the process as described above for inserting zirconium (or other similar elements).

This improvement provides that the atmosphere contains a gaseous compound of a modifier metal (e.g., zirconium) which decomposes on contact with the substrate and deposits the modifier metal thereon simultaneously with the deposition of aluminum.

In contrast, neither Darolia nor Wachtell (whether alone or in combination) teach or suggest the noted recitations in claim 1 as described above.

Darolia discloses a process for coating the internal passage of a gas turbine component with a nickel aluminide modified by an element selected from the group consisting of hafnium,

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yttrium, zirconium, chromium and silicon, the average concentration of which is between about 0.1 to about 5.0 percent.

The coating of the external surface of the gas turbine component is considered as optional.

The principle of this coating is based on the use of a sealed box containing a precursor and an activator gas, this box communicating with flow channels which also communicate with the internal passages of a turbine component (see Figure 4 and corresponding description from column 6, line 41 of Darolia).

Here, the gases are directed to pass through said internal passages to escape, thus allowing it to coat all the inside of the turbine component.

The outside of said component may be coated with a coating of the type MCrAlX wherein M represents nickel, cobalt, iron, and their alloys and X is an element such as hafnium, zirconium, yttrium, tantalum, rhenium, platinum, silicon, titanium, boron, carbon and their alloys. Examples of such compositions are NiAlCrZr and NiAlZr.

According to the process of Darolia, aluminum and a modifier element are deposited through different techniques such as chemical vapor aluminiding. The preferred source of aluminum is gaseous. For this purpose, there is used a donor consisting of metallic aluminum, an aluminum alloy (powder of TiAl or granules of chromium aluminum) or a compound containing aluminum, a source of the modifier element and a halogenated activator such as aluminum chloride, aluminum fluoride or ammonium fluoride, such salts being placed within the reaction chamber.

The source of zirconium is either a zirconium powder or zirconium chloride. The activators and the halogenated gas, containing or not the modifier elements, are in contact with the aluminum alloy and the source of the modifier element to form the desired halogenated gas. Besides aluminiding by vapor deposition, the coating of the internal passages may be obtained by chemical vapor deposition (CVD), slurry-coating, foam coating, organo-metallic chemical vapor deposition, pack cementation, and above - the - pack aluminiding (column 7, lines 55-60).

After the coating step of the internal passages, the outside of the component may be protected. It is recommended for the process in Darolia to apply a coating of the type MCrAlX as mentioned above. This coating may be surmounted by a layer of ceramic, preferably yttria-stabilised zirconia (column 8, lines 8-18).

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Wachtell relates to a conventional cementation pack. The donor is a powder of CrAl whose aluminum content is between 3 and 20 % by weight and the activator is a vaporizable halogen.

Wachtell also adds ingredients made of an alloy composed of aluminum, beryllium, boron, carbon, chromium, cobalt and refractory metals and alloys thereof in order to control the aluminum flux.

Thus, according to Wachtell, aluminum, chromium, iron, silicon and their mixtures may be deposited.

The Examiner contends that it would have been obvious to one having ordinary skill in the art at the time of this application was filed to have used the pack cementation / contact method disclosed in Wachtell in the overall method disclosed by Darolia with a reasonable expectation success as Darolia and Wachtell teach that such methods are known to be so capable.

However, both Darolia and Wachtell teach conventional methods according to the prior art, and the combination of such documents does not render this invention obvious. That is, it is **not at all obvious** that a gaseous compound of a modifier metal could act as an activator for the positing of the modifier metal **simultaneously** with the deposition of aluminum. (See also arguments below with respect to claim 5).

At least for the reasons explained above, the Applicant respectfully submits that a *prima facie* case obviousness has not been established for claim 1 because Darolia and Wachtell do not teach or suggest all the claim limitations of claim 1. As such, the Applicant respectfully request that the rejection of claim 1 be withdrawn and that this claim be allowed.

Dependent claims 2-23 depend (directly or indirectly) from claim 1. As such, these dependent claims incorporate all the terms and limitations of claim 1 in addition to other limitations, which together further patentably distinguish them over the references made of record.

In addition, regarding claim 5, the Examiner contends that it would have been obvious to have used an active gas comprising a single gaseous compound that is both an activator halide and a source of the modifying element in the process disclosed by Darolia with a reasonable expectation of success. The Applicant respectfully disagrees with the contention. That is, as a matter of fact, Darolia makes a distinction between the activator of the modifier metal donor; "...

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and a halide activator, preferably aluminum chloride, aluminum fluoride or ammonium fluoride are placed into the source chamber ... " (column 7, lines 9 and 10).

By contrast, in the present application, it is taught that the donor of the modifier metal may constitute both activators ("the zirconium salts which are capable of acting as an activator include zirconium chloride $ZrCl_4$, zirconium oxichloride $ZrOCl_2$ and ammonium fluoroaluminate $(NH_4)_2ZrF_6$, this list not being restrictive. All these salts have the advantage of being gases above $250^\circ C$. For reasons of convenience and safety, it is advantageous to use zirconium oxichloride.")

The fact that the modifier metal halide could act as an activator was far from being obvious, and may actually be taught away by Darolia.

In addition, as a matter of fact, it was well known to a person skilled in the art that the amount of deposited aluminum depends on the amount of activator added to the donor cement (the aluminum alloy) up to a given limit which is imposed by thermodynamics.

The Al equilibrium (of the solid donor : chromium aluminum or chromium titanium alloy) with the gases formed (Al_2X_6 , AlX_3 / AlX_2 / AlX , where X is chloride and/or fluoride) may be easily calculated with softwares. With such calculation, it is clear that the predominant species are Al_2X_6 and AlX_3 , whereas only AlX decomposes to give aluminum at the substrate surface (such a reaction is spontaneous).

It is this aluminum which combines with nickel to form β -NiAl. As there is an equilibrium between the various gases formed within the deposit box, the amount of aluminum halide will depend on the amount of the halide introduced, whatever its form may be (ammonium halide which decomposes above $300^\circ C$ into nitrogen, hydrogen and halogenated acid, aluminum halide ...).

If, as taught by Darolia, the donor of the modifier metal is mixed with the activator, there will be a competition between formation of aluminum halide and stability of the modifier metal halide. The predominant species will always be the aluminum halides and the contents of Zr of the coating will be very low as shown by example 3 (see also Figure 2) of this application.

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Under such circumstances, it will be impossible to obtain an average concentration in zirconium of the order of 1000 ppm and more.

Regarding claim 8, the Applicant respectfully disagrees with the Examiner's assertion that, in the case of zirconium, aluminum is partially replaced by the modifier metal. That is, as a matter of fact, if reference is made to the ternary diagram AlNiZr, there is no monophasic domain where zirconium could be substituted.

Regarding claim 9, it is true that any aluminizing gives β -NiAl, but what is inventive in the instant process is to obtain such a phase with an activator containing zirconium.

Regarding claim 18, the objection is now overcome in view of the amendment of claim 1.

Regarding claims 19, the Examiner contends that Darolia teaches a process according to claim 1, in which the substrate and the precursor are located in an enclosure permitting only limited exchanges with the exterior. The Applicant respectfully disagrees with this contention. That is, as a matter of fact, according to Darolia, the communication toward outside is made through the internal passage of the component. This is not a semi-sealed chamber as in this invention.

Claims 20, 22, and 23 have been each amended to remove the "preferably" language. In addition, the range disclosed by Darolia does not fall within the range as recited in amended claim 22 in which the said concentration of the modifier metal by mass lies at or above 500 ppm and below 1000 ppm. Furthermore, Darolia does not provide in which the said high temperature is about 1080°C.

Regarding claim 21, the range disclosed by Darolia does not fall completely within the range of this claim.

The Examiner also rejects claims 16 and 17 as being unpatentable over Darolia and in view of Fournes et al. (US Patent No. 5,068,127). However, the addition of Fournes does not make up for the deficiency as described above with respect to Darolia.

New claim 24 should be patentable over references made of record for its recitations of a method for forming a protective coating containing aluminium on a surface of a metal substrate, the method comprising:

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placing the metal substrate and a non-gaseous precursor containing aluminium in contact, at a high temperature, with an atmosphere containing an active gas;

reacting the atmosphere containing the active gas with the non-gaseous precursor containing aluminium to form a gaseous aluminium compound;


decomposing the gaseous aluminum compound on contact with the metal substrate and depositing aluminium metal on the metal substrate, wherein the atmosphere further comprises a gaseous compound of a modifier metal; and

decomposing the gaseous compound of the modifier metal on contact with the metal substrate and simultaneously depositing the modifier metal on the metal substrate with the depositing of the aluminium metal (emphasis in underline added).

Dependent claim 25 depends from claim 24. As such, this dependent claim incorporates all the terms and limitations of claim 24 in addition to other limitations, which together further patentably distinguish them over the references made of record.

In view of the foregoing, the Applicant respectfully submits that Claims 1-25 are in condition for allowance. Reconsideration and withdrawal of the rejections are respectfully requested, and a timely Notice of Allowability is earnestly solicited. If there are any remaining issues that can be addressed over the telephone, the Examiner is encouraged to call the Applicants' attorney at the number listed below.

Respectfully submitted,
CHRISTIE, PARKER & HALE, LLP

By 

Peter C. Hsueh
Reg. No. 45,574
626/795-9900

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